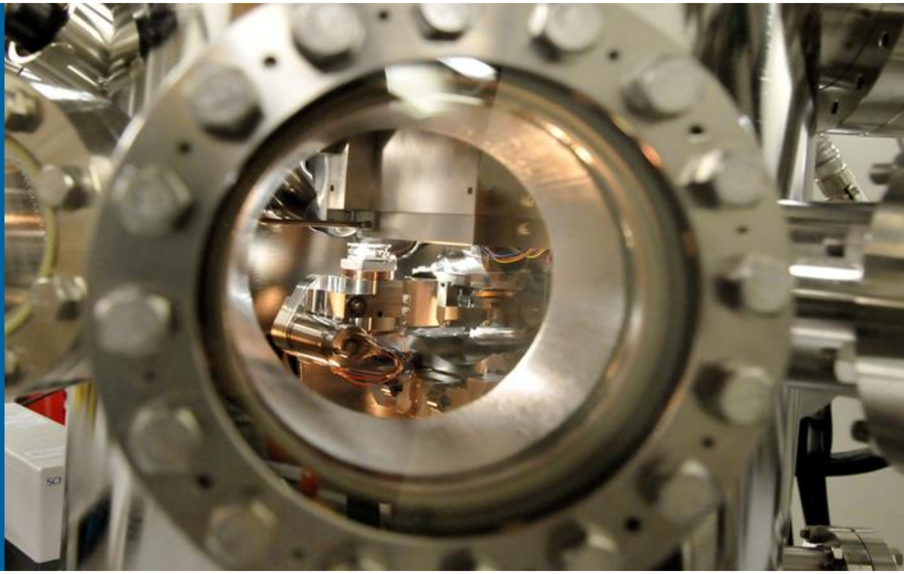
PROJECT ID: BAT166

POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS



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DOE Annual Merit Review
Washington, DC, June 10-13, 2019

POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS

Overview

TIMELINE

- Project start: October 1, 2015
- Project end: September 30, 2018
  - 100% complete

OBJECTIVES

- Elucidate physical and chemical response of constituent battery materials under battery abuse conditions
- Develop analysis procedures

BUDGET

- FY18: $850K
- FY17: $850K
- FY16: $750K

COLLABORATORS

- Oak Ridge National Laboratory
- Sandia National Laboratory

A THREE-LABORATORY CONSORTIUM

- Argonne, Sandia and Oak Ridge teamed to leverage strengths and abilities at each site to study effects of processing and abuse response of two lithium-ion battery chemistries, high-Ni NMC and $LiFePO_4$
- What each site contributes
  - Argonne: Post-test Facility – ability to characterize battery materials under inert atmosphere
  - Sandia: Battery Abuse Testing Lab (BATLab) – ability to thermally and electrically abuse cells under controlled conditions
  - Oak Ridge: Battery Manufacturing R&D Facility – ability to make cells with well-defined chemistries, as the project needs

POST-TEST ANALYSIS OF LITHIUM-ION BATTERY MATERIALS

Relevance

Science Issues

- What are the underlying changes in cell components during an abuse event, such as overcharge? Are there effects from battery format? Chemistry? How do these effects manifest themselves?
  - In principle, we can use what we learn to mitigate the effect of abuse
- What is the impact of processing methods on the performance of the cells? That is, what is the effect of type of binder and drying procedure on the SEI layer, cell impedance, binder degradation, gases, and current collector corrosion?

APPROACH

- Changes in cell components during overcharge
  - Compare surface and bulk chemistry of electrodes before and after abuse event
  - Expected outcome
    - Understanding of the physical and chemical changes in the cell during abuse events
    - Design rules to manage/eliminate abuse consequences, such as binders for a more-controlled overcharge response
- Effect of formation protocol
  - Compare electrochemical performance of cells formed with “fast” and “slow” protocols
  - Impact of protocol on electrode surface structure and chemistry

MILESTONES

Milestone	Due date	Type	Status
Report to DOE	12/31/15	Quarterly progress measure	Complete
Report to DOE	3/31/16	Quarterly progress measure	Complete
Report to DOE	6/30/16	Quarterly progress measure	Complete
Compare aqueous- and organic-processed electrode, elucidating differences.	9/30/16	Annual SMART milestone	Delayed. Initial comparison showed a difference in reactivity
Report to DOE	12/31/16	Quarterly progress measure	Complete. 9/30 milestone delayed due to XPS issues. Should be complete in January
Report to DOE	3/31/17	Quarterly progress measure	Complete. 9/30 milestone complete
Report to DOE	6/30/17	Quarterly progress measure	Complete
Compare pre- and post-abuse event cell materials, elucidating changes in electrode materials	9/30/17	Annual SMART milestone	Complete
Report to DOE	12/31/17	Quarterly progress measure	Complete
Report to DOE	3/31/18	Quarterly progress measure	Complete
Report to DOE	6/30/18	Quarterly progress measure	Complete
Compare effect of formation protocol on cells containing Si/Graphite electrodes	9/30/18	Annual SMART milestone	Complete

TECHNICAL PROGRESS

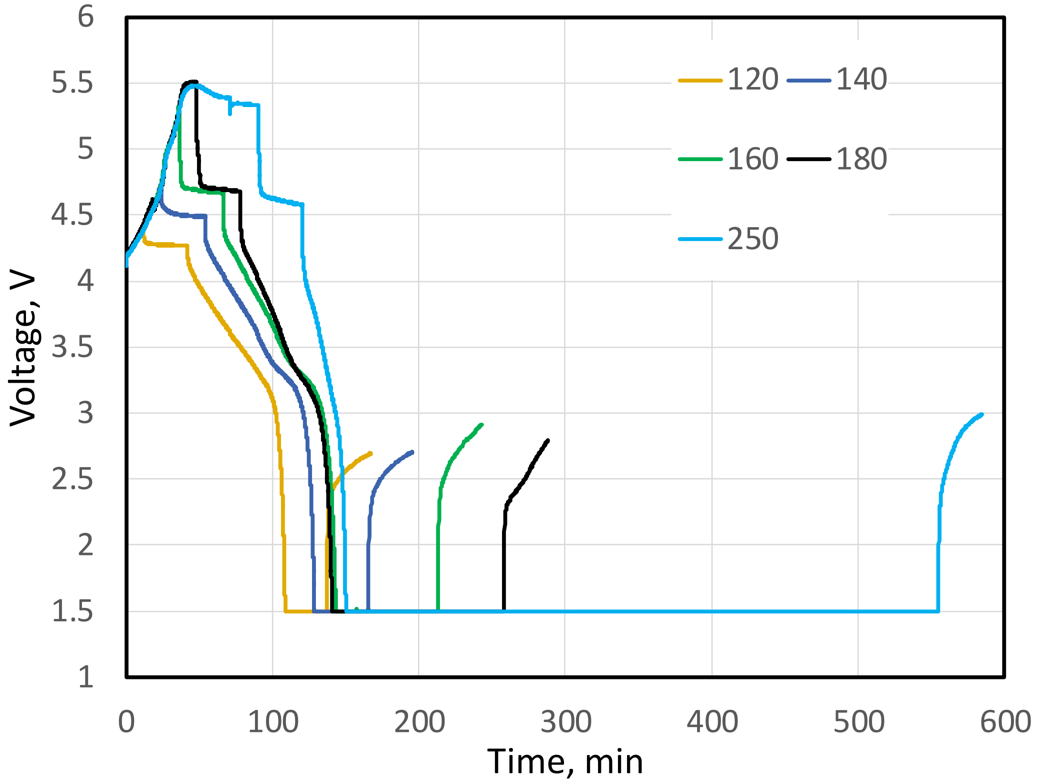
- The DOE Battery Manufacturing R&D Facility at ORNL (BMF) made NCM/Silicon-Graphite (15 wt% Si) pouch cells, using Li-PAA Binder and Gen2 electrolyte+10 wt% FEC

- Two experiments
  1. The Battery Abuse Testing Laboratory at SNL charged each cell to a different state of overcharge, from 100% SOC (No overcharge) to failure
  2. Cells were formed using “Fast” and “Slow” protocols. They were cycled at Argonne to determine relative electrochemical performance

- The cells were disassembled at Argonne and their components characterized To elucidate the physicochemical changes caused by the experiments

OVERCHARGING CELLS CONTAINING SI/GRAPHITE COMPOSITE ELECTRODES

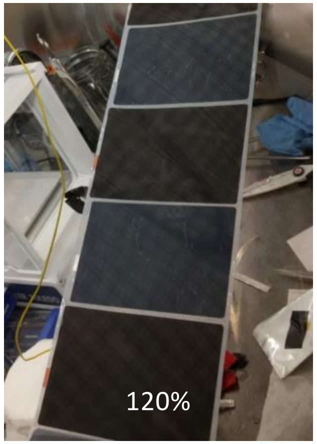
- After the overcharge experiment at SNL, the cells were discharged to about 3.0 V. The cells were subsequently discharged to about 1.5 V to minimize their residual energy for safe handling. If the voltage rose above 3.0 V, a subsequent discharge to 1.5 V was performed and the rest step was repeated

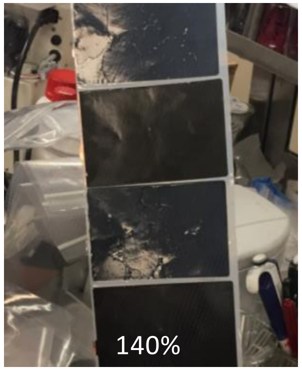


OPTICAL PHOTOGRAPHS OF ANODES AFTER OVERCHARGE

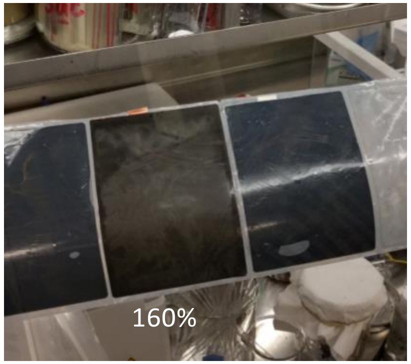
Glove box images

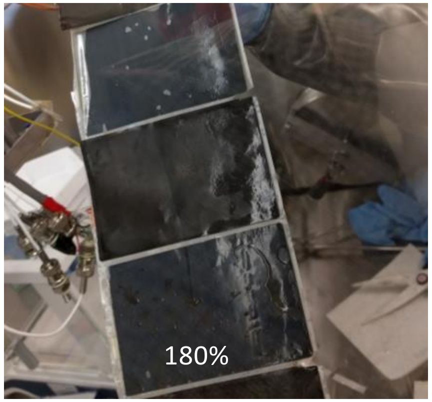
- The number at the bottom of each image is the state of charge that each electrode experienced. Failure occurred ~250%





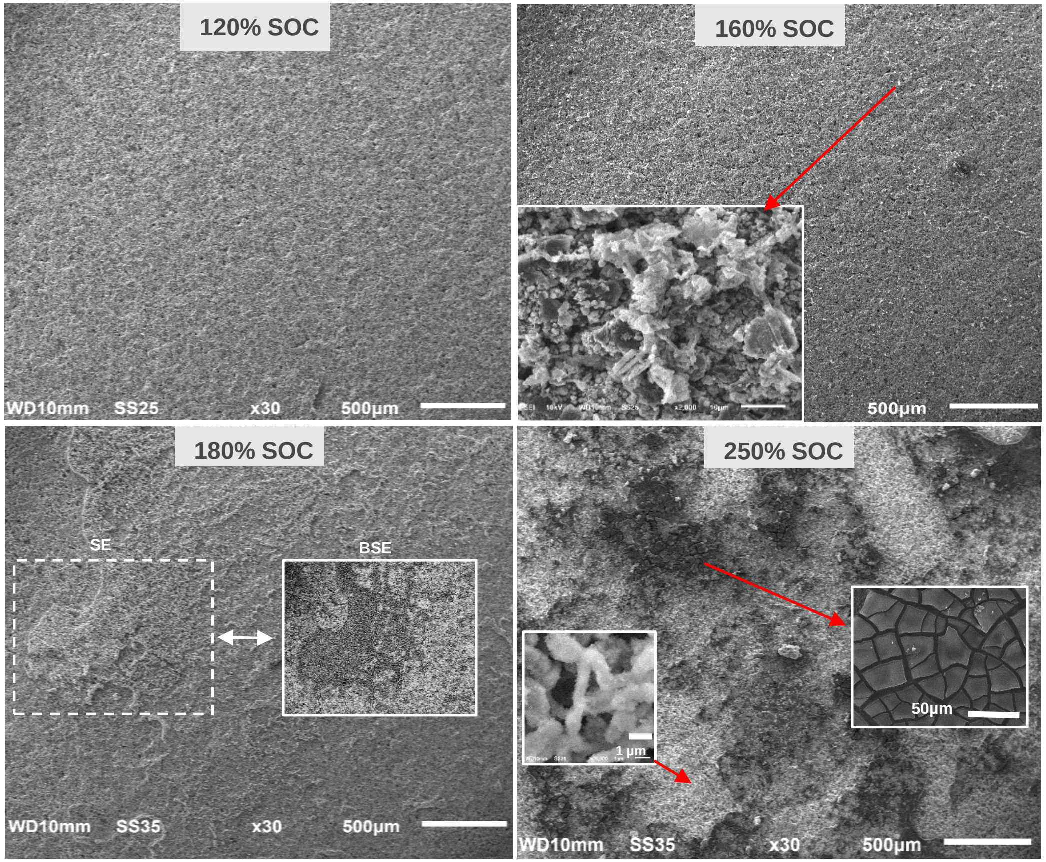
- Not much change was seen until failure



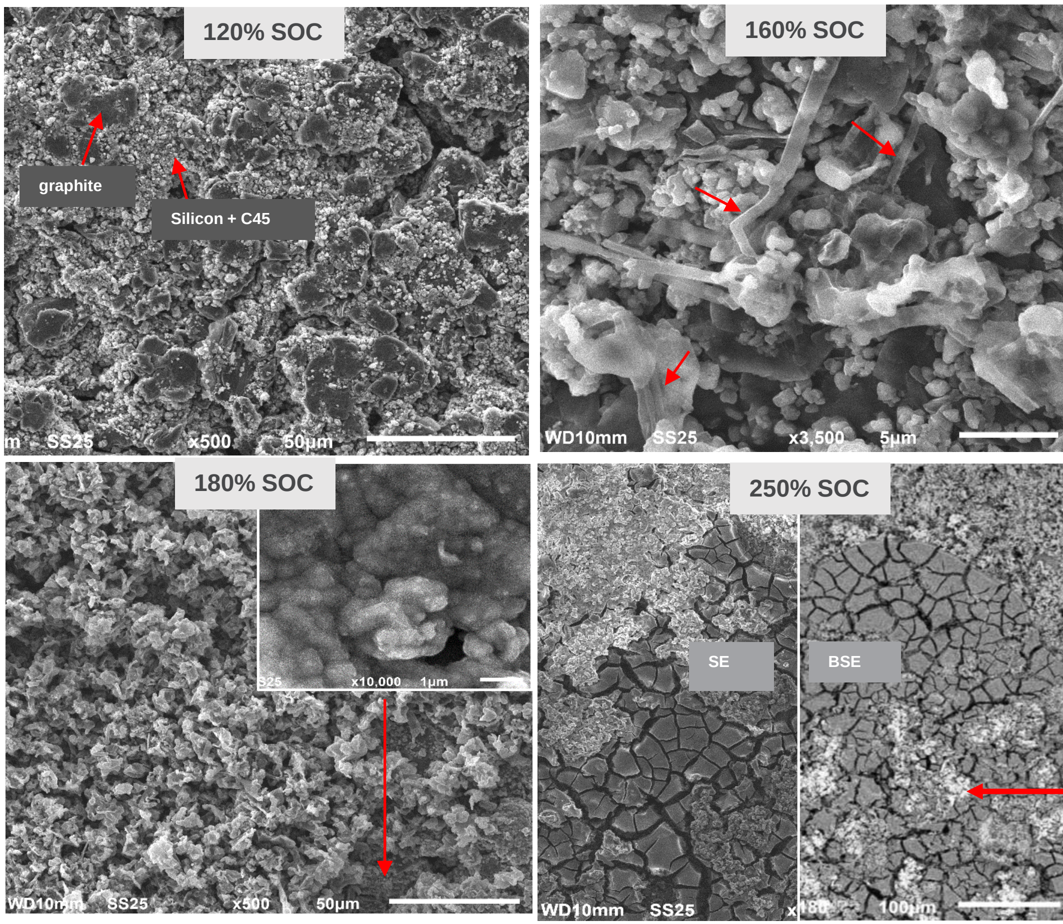


SCANNING ELECTRON MICROSCOPY (SEM) REVEALS NO CHANGES AT LOW SOCS

- SEM revealed no discernable changes on the 100, 120, and 140% SOC anodes



SEM OBSERVATION REVEALS CHANGES WERE SEEN AT HIGHER SOCS



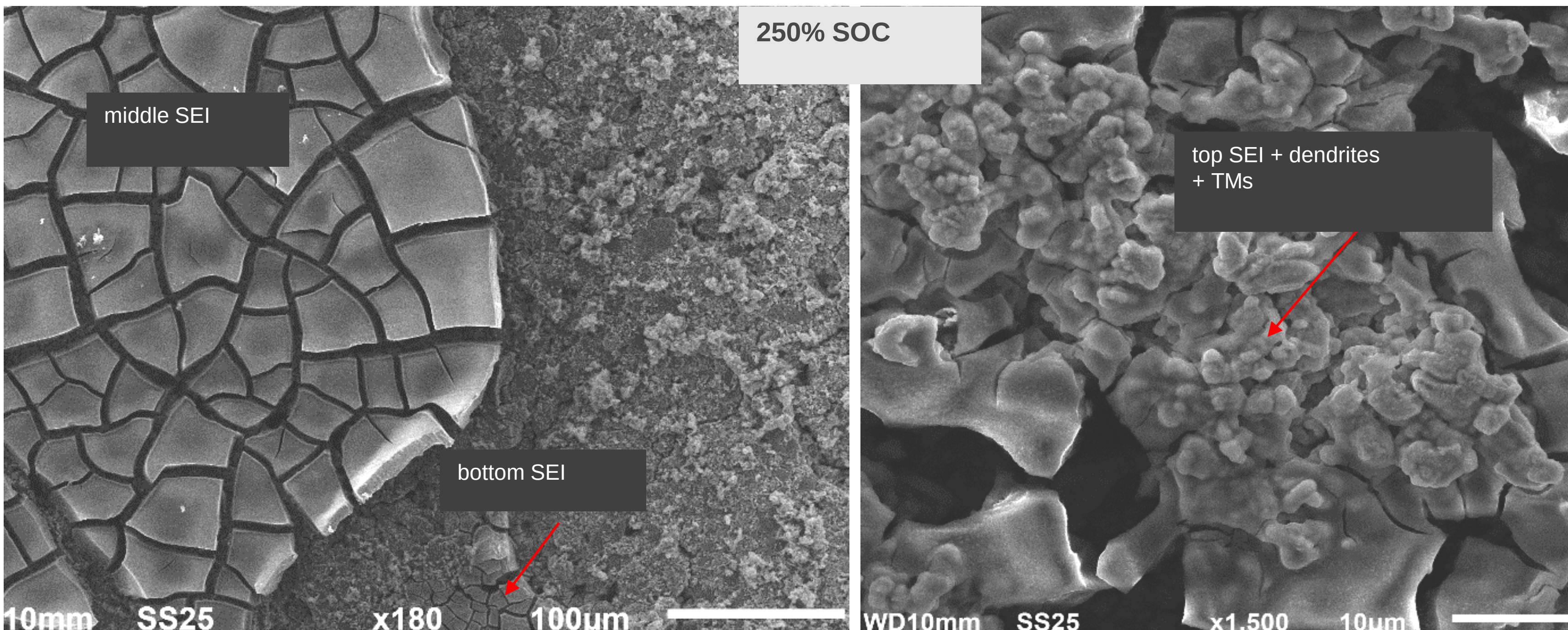
- At 160% SOC, some dendrites and a film were seen
- At 180% SOC, the dendrites were longer
- At 250% SOC, the surface was very reacted. It was covered with an SEI layer and coated dendrites

Particles of, possibly, transition metals

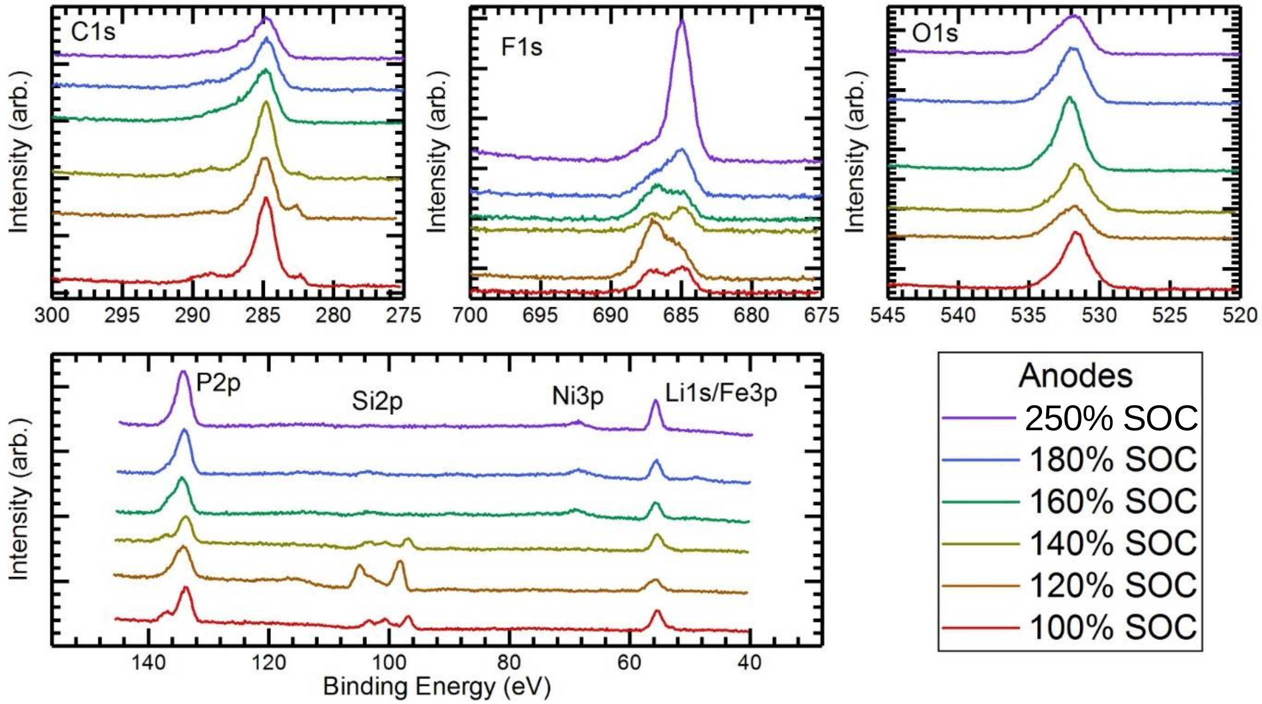
THE SEI LAYER CAN BE COMPLEX

250% SOC

- At very high SOCs, the SEI layer consisted of two major components, top, middle, and bottom layers
- The top layer had dendritic material and transition metals on/in it



X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) SHOWS COMPOSITION OF SURFACE LAYER



Correlations in the data

Data set	Slope (s. e. e.)	Intercept (s. e. e.)	r^2
SOC/Li	7.46 (1.43)	7.60 (2.38)	0.99
SOC/F	9.43 (5.10)	-2.77 (8.78)	0.88
SOC/C	-12.89 (4.27)	56.75 (7.56)	0.99
Li/F	1.46 (0.60)	-17.01 (12.21)	0.89

SEI layer is rich in LiF

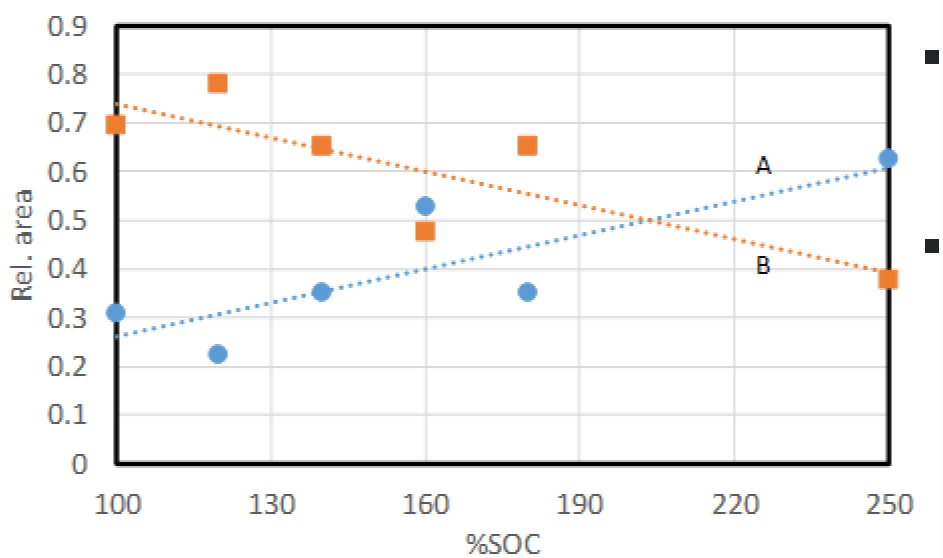
s.e.e= standard error of the estimate

FOUR ORGANICS WERE OBSERVED AS PART OF THE SEI LAYER

High Performance Liquid Chromatography

- Four organic compound were observed

Compound	Parent ion, Da	Proposed formula	Calc'd weight, Da	Proposed structural formula
A	368	$[C_{18}H_{31}O_6]^+$	368.2	$[CH_3CH_2CH{=}CHO(CH_2CH_2O)_3(CH{=}CHO)_2CH{=}CH_2CHCH_3]H^+$
B	387	$[C_{18}H_{36}O_7Na]^+$	387.5	$[CH_3CH{=}CHO(CH_2CH_2O)_6CH_2CH_2CH_3]Na^+$
C	352	?		
D	352	?		

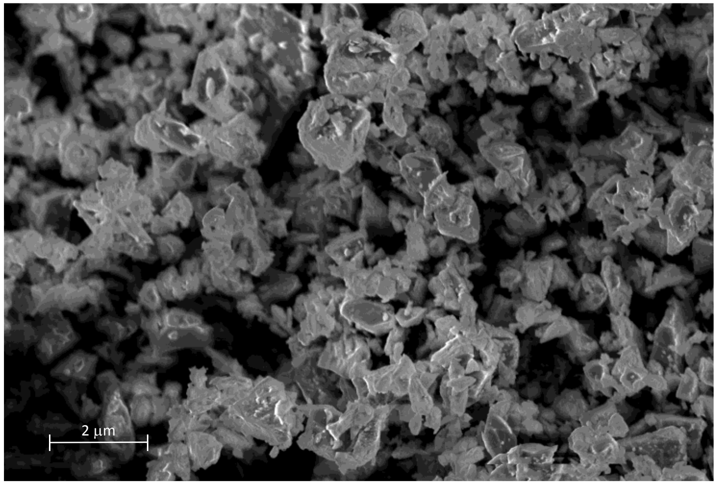


- The relative amount of A increases with SOC, while the amount of B decreases
- The observed molecular ions were smaller in the silicon-containing case than those found in pure graphite. In addition, the proposed molecular structures in the silicon-containing electrode tended to be unsaturated polyethers.

EFFECT OF FORMATION PROTOCOL: SI/GRAPHITE COMPOSITE ELECTRODE

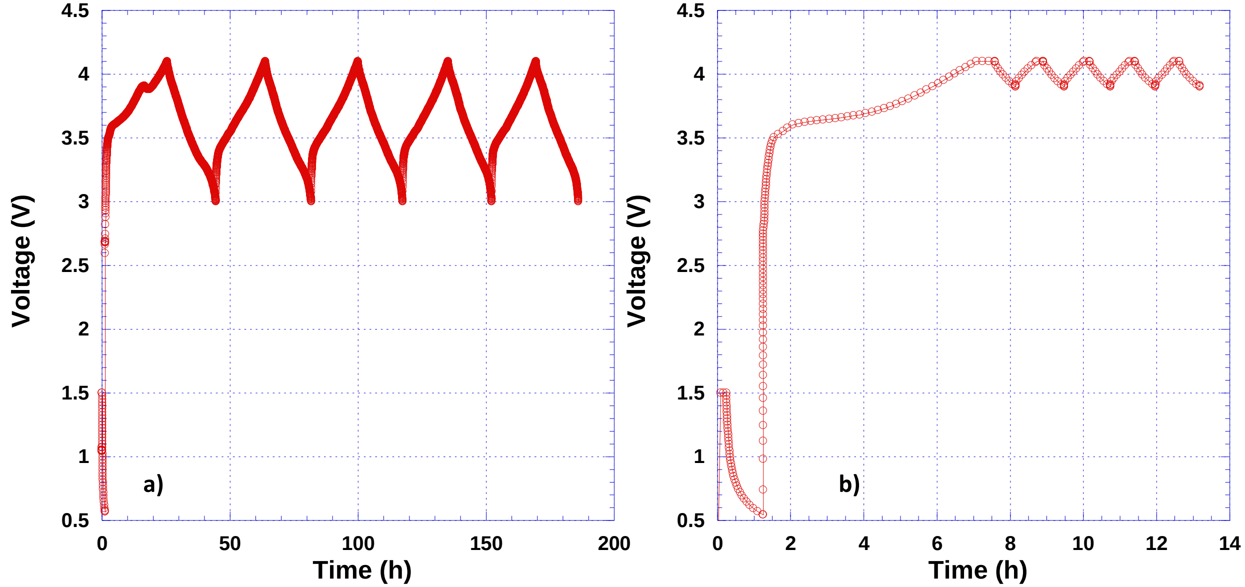
- Two formation protocols were evaluated
  - **Slow**: Five cycles at the C/20 rate between 4.1 and 3.0 V
  - **Fast**: Five cycles constant-current/constant voltage at the C/5 rate with a tap current of C/20 between 3.9 and 4.1 V, based on the hypothesis that most of the SEI forms at high voltage

- After formation, all cells were cycled 100 times at the C/1 rate between 4.1 and 3.0 V at 30°C



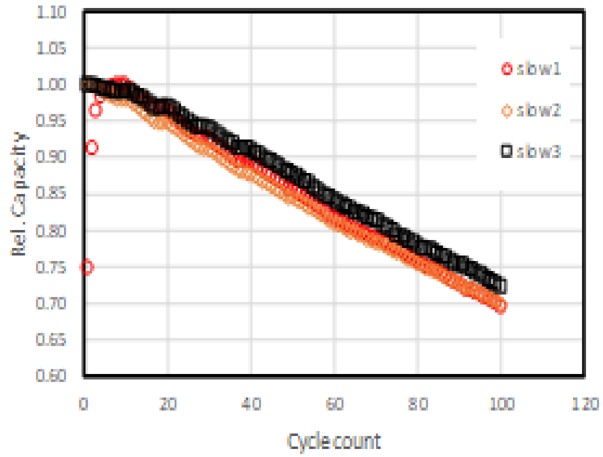
- SEM image of the silicon used in this experiment. Although the particle size was reported to be in the range of 70-130 nm, there were clearly some bigger particles.

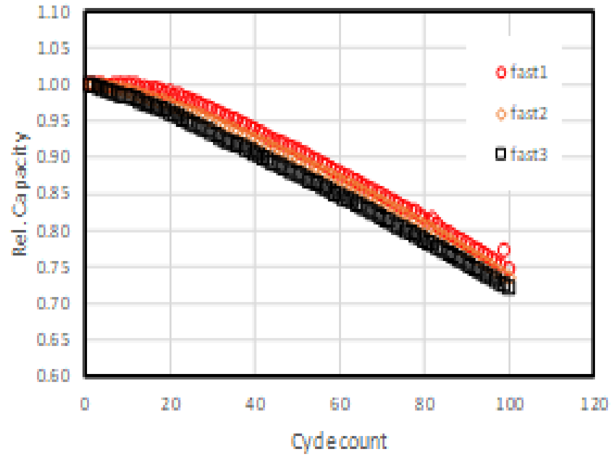
VOLTAGE VS. TIME CURVES DURING FORMATION SHOW DIFFERENCES

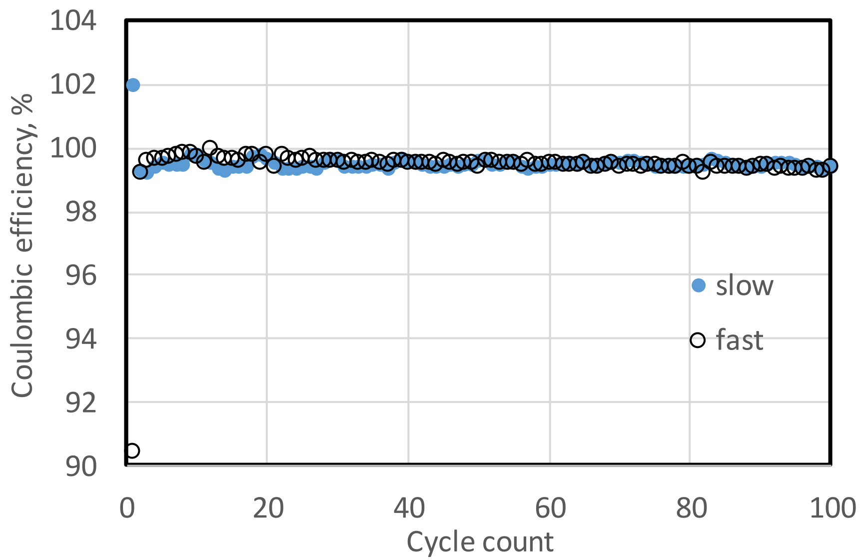


- Slow formation (a) took 186 h to complete and fast formation)b) took 13.2 h to complete

NO SIGNIFICANT DIFFERENCES WERE SEEN IN CYCLING BEHAVIOR







XPS SHOWS EFFECT OF FORMATION PROTOCOL

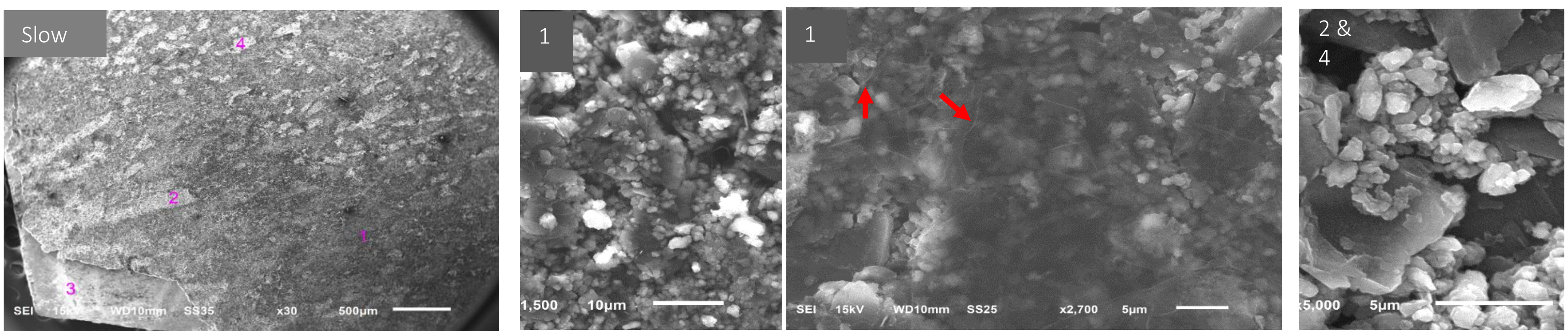
- Composition of surface material on the anodes. The average, estimated uncertainty is ~10% of the value reported

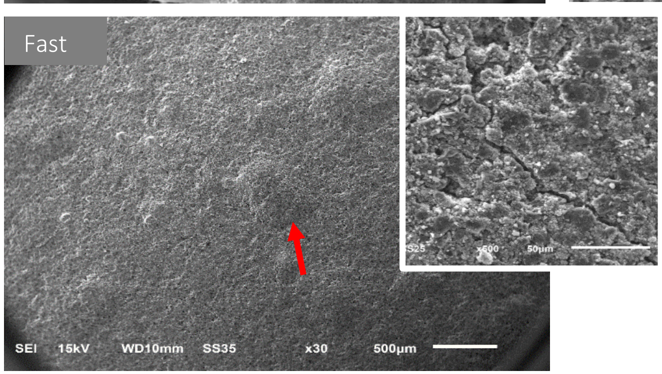
	Composition, at.%								
Formation	C	O	Li	F	P	Ni	Al	Cu	Si
Slow	24.41	29.59	29.78	11.58	1.59	0.28	2.06	0.20	0.52
Fast	22.94	36.67	33.53	5.83	0.54	0.15	0.32	0.00	0.00

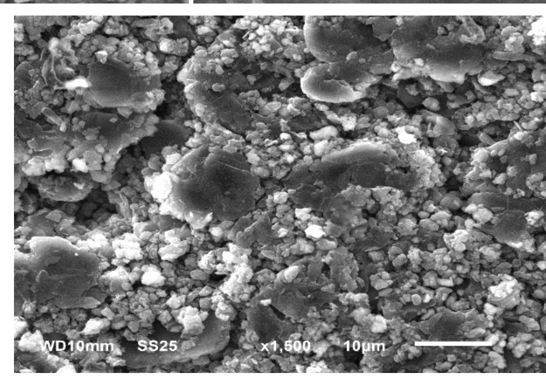
- Concentrations of F, P, Ni and Al are two times or more higher on the anode from the slow formation protocol. May be due to greater amount of electrolyte decomposition
- Based on the XPS spectra, the fluorine may be in the form of LiF. Additionally, there were two phosphorus environments in the slow protocol cell and only one in the fast protocol one

ADDITIONAL IMPACT OF FORMATION PROTOCOL WAS SEEN IN THE SEM

- The anode surface from the slow process had a mottled appearance. The darker area (#1 in top row) was covered with a thin film (red arrows). The lighter areas (#2 and 4) did not show a film, which may have come off onto the separator during disassembly
- The surface from the fast protocol anode surface had large bubbles (see red arrow in bottom row), indicating gas buildup. Cracks were seen on top of bubbles (inset). The active layer had better adherence to the current collector than the slow protocol active layer







Oak Ridge National Laboratory
Sandia National Laboratories
Argonne National Laboratory

SUMMARY/CONCLUSIONS

- Argonne, Oak Ridge and Sandia National Laboratories are collaborating to study the physical and chemical effects of overcharge on cells, and the influence of formation protocol
- Overcharge
  - Characterization of the Si/graphite electrode showed attributes similar to those found in a pure graphite electrode. In part, this was not unexpected, since silicon represented a relatively small fraction of the total electrode, ~15 wt%. The effect of silicon was seen in the composition of the SEI layer and the trends in two components of the SEI layer. One of the SEI components increased with % SOC, and the other decreased. The observed molecular ions were smaller in the silicon-containing case than those found in pure graphite. In addition, the proposed molecular structures in the silicon-containing electrode tended to be unsaturated polyethers
- Formation Protocol
  - Both the slow and fast formation protocols yielded cells with similar performance characteristics. The SEI layers in both cells, even though different in chemistry, were stable and functioned analogously. The fast protocol may thus provide a more economical route to cell fabrication

PUBLICATIONS

Effect of overcharge on lithium-ion cells containing Li($Ni_{0.5}Mn_{0.3}Co_{0.2}$)O_2 cathodes: NMP-soluble binder. I. Microstructural Changes in the Anode, Nancy Dietz Rago, Javier Bareno, Ira Bloom, Jianlin Li, David L. Wood, III, Leigh Anna Steele, Joshua Lamb, Scott Spangler, Christopher Grosso, Kyle Fenton, J. Power Sources, <u>385</u> (2018) 145-155. DOI: 10.1016/j.jpowsour.2018.01.009

Effect of overcharge on lithium-ion cells containing Li($Ni_{0.5}Mn_{0.3}Co_{0.2}$)O_2 cathodes: NMP-soluble binder. II — Chemical changes in the anode, Ira Bloom, Javier Bareno, Nancy Dietz Rago, Fulya Dogan, Donald G Graczyk, Yifen Tsai, Seema R Naik, Sang-Don Han, Eungje Lee, Zhijia Du, Yangping Sheng, Jianlin Li, David L Wood III, Leigh Anna Steele, Joshua Lamb, Scott Spangler, Christopher Grosso, Kyle R Fenton, J. Power Sources, <u>385</u> (2018) 156-164. DOI: 10.1016/j.jpowsour.2017.12.015

Effect of overcharge on NMP-processed Li($Ni_{0.5}Mn_{0.3}Co_{0.2}$)O_2 / Graphite lithium ion cells with PVDF binder. III — Chemical changes in the cathode, Javier Bareño, Nancy Dietz Rago, Fulya Dogan Key, Donald Graczyk, Yifen Tsai, Seema Naik, Sang Don Han, Eungje Lee, Zhijia Du, Yangping Sheng, Jianlin Li, David Wood , Leigh Anna Steele, Joshua Lamb, Scott Spangler, Christopher Grosso, Kyle Fenton, Ira Bloom, J. Power Sources, <u>385</u> (2018) 165-171, DOI: 10.1016/j.jpowsour.2017.12.061

Effect of overcharge on Li($Ni_{0.5}Mn_{0.3}Co_{0.2}$/Graphite cells – IV. Effect of binder on microstructural changes in the anode, Nancy Dietz Rago, Jianlin Li, Zhijia Du, David L. Wood III, Leigh Anna Steele, Joshua Lamb, Scott Spangler, Christopher Grosso, Kyle Fenton, Ira Bloom, in preparation

Effect of overcharge on Li($Ni_{0.5}Mn_{0.3}Co_{0.2}$/Graphite cells. – V Impact of binder on anode surface chemistry, Ira Bloom, Nancy Dietz Rago, Donald G. Graczyk, Yifen Tsai, Seema R. Naik, Jianlin Li, Zhijia Du, Yangping Sheng, David L. Wood, III, Leigh Anna Steele, Joshua Lamb, Christopher Grosso, and Kyle Fenton, in preparation

PUBLICATIONS (CONT'D)

Effect of overcharge on lithium-ion cells. VI – Electrode Cross-talk, Ira Bloom, Nancy Dietz Rago, Donald G. Graczyk, Yifen Tsai, Seema R. Naik, Jianlin Li, Zhijia Du, Yangping Sheng, David L. Wood, III, Leigh Anna Steele, Joshua Lamb, Christopher Grosso, and Kyle Fenton, in preparation

Effect of Overcharge on Lithium-Ion Cells: Silicon/Graphite Anodes, Ira Bloom, Nancy Dietz Rago, Yangping Sheng, Jianlin Li, David L. Wood, III, Leigh Anna Steele, Joshua Lamb, Scott Spangler, Christopher Grosso, and Kyle Fenton, J. Power Sources, submitted.

Effect of Formation Protocol: Cells Containing Si-Graphite Composite Electrodes, Nancy Dietz Rago, John K. Basco, Anh Vu, Jianlin Li, Kevin Hays, Yangping Sheng, David L. Wood, III, and Ira Bloom, J. Power Sources, submitted.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the U. S. Department of energy (DOE), vehicle technologies office. Argonne national laboratory is operated for DOE office of science by uchicago argonne, LLC, under contract number DE-AC02-06CH11357.

The work at oak ridge national laboratory, managed by ut battelle, llc, for the u.S. Department of energy (DOE) under contract DE-AC05-00OR22725, was sponsored by the office of energy efficiency and renewable energy (EERE), vehicle technologies office, applied battery research.

Sandia national laboratories is a multi-mission laboratory managed and operated by national technology and engineering solutions of sandia, llc, a wholly owned subsidiary of honeywell international, inc., For the U.S. Department of energy's national nuclear security administration (NNSA) under contract DE-NA0003525.

The authors are grateful to P. Faguy and D. Howell (VTO/DOE) for their support